

and by the bending of the N2 and C3 moieties (defined by the dihedral angle between N1, C6, and N2 and N3, C3, and N4). In complexes **3**, **5**, and **8** the metal atom is accommodated in the cavity supplied by the aromatic rings, the M-N₄ distances (Table X) showing the expected trend. The most relevant differences concern complex **8** where the presence of two coordinated tmtaa molecules produces a significant flattening of the aromatic rings and longer Zr-N₄ out-of-plane distances (Table X).

Considering the tmtaa-derived complexes so far structurally characterized, the out-of-N₄-plane of the metal seems to depend on the d configuration of the metal. Electron-rich metals are almost in the plane, and the saddle-shape conformation almost disappears. A significant comparison should be restricted however to metals having the same oxidation state or coordination number but different d configuration (Table XI). The d⁰ and d¹ metals are those having the most pronounced out-of-plane and saddle-shape conformation.

The out-of-plane of the metal seems to increase with its coordination number for the same dⁿ configuration or the same oxidation state (Table XI) although much less data are available for such a comparison.

NMR spectroscopy could give, eventually, information on the structure of tmtaa complexes in solution. This notwithstanding, very rarely have NMR spectra been reported and discussed for tmtaa. The CH and CH₃ protons should be considered as a spectroscopic probe for the structure of tmtaa in solution. In ¹H NMR spectra of **6** a singlet for CH and a singlet for the -CH₃ groups were found, independently of the solvent used. For complexes **4**, independently of the solvent (CD₂Cl₂ or CD₃CN), pairs of singlets appeared for the CH and CH₃ groups, and the intensity ratio changes as a function of the solvent as well as their separation. The temperature seems not to affect such parameters. Complex **5** showed in the ¹H NMR spectrum a pair of singlets for both CH and CH₃ groups in CD₂Cl₂ and one singlet for both CH and CH₃ in CD₃CN. Such factors give rise to some hypotheses

concerning the existence in some cases of one form, or in other cases of two forms, of the complex.

The existence of two forms from the ¹H NMR spectrum should not be related to any solvation equilibrium because both in the case of **4** and **5**, two forms are observed in noncoordinating solvents and in the absence of any even weak ligand. In addition, methylene chloride solutions of **5** to which RNC or R'CN have been added did not show any binding to the metal, as seen from the IR spectrum. We never observed Lewis acid adducts of [(tmtaa)M-(Cl)₂] complexes during our reactivity studies. The present hypothesis is that the two forms observed in the ¹H NMR spectrum are two saddle-shape conformations of the ligand with a different out-of-N₄-plane distance of the metal in a slow equilibrium determined by the nature of the metal and of the solvent, independently of its binding ability. This equilibrium is not very much affected by the temperature, a small change in the intensity being observed, in the range we explored for **5** in CD₂Cl₂, that is from 233 to 290 K in CD₂Cl₂. In the case of [M(tmtaa)₂] complexes, again the separation of the CH and CH₃ signals in pairs of singlets was observed for titanium complex **7** and disappears in the case of **8** and **9**, which show a singlet for both kinds of protons independently of the solvent. In case of **7** we should invoke either the previous hypothesis, or the nonsymmetric binding of the eight nitrogen atoms derived from two tmtaa's, due to the small size of the titanium atoms.^{22b}

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-28470.90) for financial support.

Supplementary Material Available: Experimental details for data collection and refinement of the structures (Table SI) and listings of unrefined hydrogen coordinates (Tables SII-SV), anisotropic thermal parameters (Tables SVI-SIX), and bond distances and angles (Tables SX-SXIII) (18 pages); listings of observed and calculated structure factors (98 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie der Universität, W-3000 Hannover 1, FRG

Synthesis and Properties of Chloryl Chloride, ClClO₂

Holger S. P. Müller and Helge Willner*

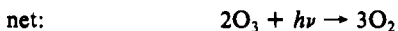
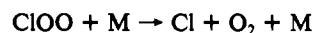
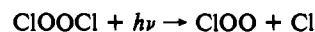
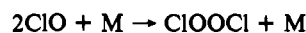
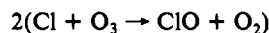
Received November 7, 1991

Halogen exchange between FClO₂ and AlCl₃, BCl₃, or HCl afforded chloryl chloride, ClClO₂, identified by IR and UV spectroscopy in noble gas matrices and in the gas phase. All six fundamental vibrations, as well as some over and combination tones of 12 isotopomers were detected for the novel chlorine oxide having C_s symmetry. Use of the product rule in the symmetry class A'' with vibrational frequencies of four independent isotopomers, in conjunction with experimental and ab initio results of related compounds, allowed the geometric parameters to be estimated (*r*(ClCl) = 222 ± 6 pm, *r*(ClO) = 144.0 ± 0.5 pm, ∠(ClClO) = 103.5 ± 1°, ∠(OCIO) = 116.0 ± 0.5°) and a force field to be calculated. The UV spectrum shows two maxima at 231 and 296 nm with σ = 1.3 × 10⁻¹⁷ and 1.5 × 10⁻¹⁷ cm² molecule⁻¹, respectively. Photolysis of matrix-isolated ClClO₂ resulted in the isomers ClOClO and ClOOCi. In the gas phase ClClO₂ decomposes into ClO₂ and chlorine, but it can also be formed by reacting Cl atoms with ClO₂. At room temperature and partial and total pressure of 1 and 4 mbar, respectively, the half-life of ClClO₂ is 1 min. The role of ClClO₂ in stratospheric chemistry is discussed in relation to possible reaction schemes.

Introduction

Chlorine-containing compounds play an important role in stratospheric chemistry.^{1,2} In particular, high concentrations of ClO and ClO₂ have been measured in the polar region during early spring.^{2,3} Thus it was suggested that strong ozone depletion occurring after sunrise could be caused by a catalytic cycle in which dimerization of ClO and by photolysis of the products are

the main steps⁴ (Scheme I). Kinetic investigations⁵ together with Scheme I



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field measurements and model calculations⁶ support this assumption.

Several ab initio calculations were performed on the isomers of Cl₂O₂ showing that ClOOCi, ClClO₂, and probably ClOCiO could be stable under stratospheric conditions.⁷⁻¹⁰ Geometric parameters, dipole moments, vibrational frequencies, and intensities for the ³⁵Cl₂¹⁶O₂ species^{7,11-13} as well as vibrational frequencies of the ³⁷Cl and ¹⁸O isotopomers,¹²⁻¹⁴ quadratic force fields,^{13,14} and UV spectra^{9,10} were calculated for these species. Several energetic aspects were investigated theoretically.^{8-10,15} Calculations on geometric parameters, and vibrational frequencies and intensities for the Cl₂O₂ isomers were also compared with those of related compounds.⁸

The first spectroscopic evidence for a Cl₂O₂ species arose from early photolysis experiments of Cl₂O isolated in nitrogen^{16,17} and argon¹⁷ matrices but the measured vibrational bands could not definitively be assigned to a certain isomer. Later several experiments were undertaken to isolate ClO and lower chlorine oxides in argon matrices.^{18,19} A band at 994.3 cm⁻¹ together with ³⁷Cl and ¹⁸O counterparts was tentatively assigned to ClOCiO.¹⁹

It has been shown recently by submillimeter wave spectroscopy, that ClOOCi is the major product of the ClO dimerization,²⁰ but the formation of other isomers of Cl₂O₂ cannot be excluded. Thus, UV spectra of the ClO dimerization products are mainly due to ClOOCi.^{21,22} In the infrared region, very weak bands near 750 and 650 cm⁻¹, in a matrix²³ as well as in the gas phase,²² were attributed to ClOOCi on the basis of ab initio calculations.⁷

Several attempts to prepare chloryl chloride, ClClO₂, were undertaken in the 1950s: reactions of chloryl fluoride, FClO₂, or chloryl perchlorate, ClO₂ClO₄, with NOCl, NO₂Cl, AlCl₃, BCl₃, HCl, etc. resulted in the expected fluorine-containing byproduct, as well as ClO₂ and Cl₂ in a 2:1 ratio, suggesting decomposition of the desired ClClO₂.²⁴⁻²⁷ The ClClO₂ molecule was also

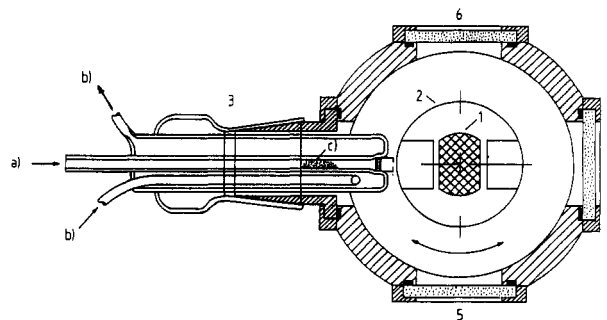


Figure 1. Schematic representation of the matrix-isolation assembly: 1, matrix support; 2, radiation shield; 3, deposition assembly (a) from the vacuum line, (b) temperature control (with ethanol), (c) AlCl₃ powder; 4, CsI window; 5, TPX window; 6, quartz window.

postulated by ³⁸Cl labeling studies as an intermediate in the formation of ClO₂ in aqueous solutions containing chlorite or chlorate.²⁸

We have investigated ClClO₂ in noble gas matrices and in the gas phase for the first time. While certain of our results were presented earlier,²⁹ an extended description is presented here.

Experimental Section

Chemicals. *Caution!* Although no explosion occurred during our studies, chlorine oxides are potentially explosive, especially in the presence of organic material. They should be handled only with proper safety precautions and in millimolar quantities.

FClO₂ was prepared in a modification of the original method³⁰ by reacting 10 mmol of ClO₂ with a slight excess of F₂ (6 mmol) in a 500-mL glass bulb for 16 h at 255 K. Excess F₂ was pumped off at 77 K, and the product was purified by fractional condensation (77 K/155 K/190 K). Traces of SiF₄ and FClO₃ were the only byproducts trapped at 77 K, while the 155 K trap contained pure FClO₂. The 190 K trap contained traces of ClO₂BF₄, which slowly decomposes to FClO₂ and BF₃ at room temperature. On the basis of ClO₂, the yield was about 90%. Although FClO₂ might be handled in a well-dried glass vacuum system, a metal vacuum system is preferred to avoid reaction with glass,²⁴ especially in the course of matrix isolation studies. ¹⁸O-Enriched FClO₂ was prepared from ¹⁸O-enriched ClO₂ and F₂ in the way described above.

ClO₂ was produced from KClO₃, oxalic acid, and dilute sulfuric acid.³¹ ¹⁸O-Enriched ClO₂ was synthesized by hydrolysis of ClF₃ with H₂¹⁸O (99% ¹⁸O; Johnson Matthey): H₂¹⁸O (1 mL, 50 mmol) was transferred into a Teflon-PFA reactor (30 mL; Fluoroware). After the water was degassed, 1 mmol of ClF₃ was condensed into the reactor at 77 K. While shaking, the reactor was allowed to warm up to room temperature and maintained at this temperature for 5 min. O₂ was pumped off at 77 K. The volatile reaction products were condensed into a glass trap containing dry KF to remove HF.

Fractional condensation (77 K/170 K/210 K) yielded pure ClO₂ in the 170 K trap. The 77 K trap contained Cl₂ and small amounts of FClO₃ and ClO₂. The hydrolysis of 1-mmol portions of ClF₃ was repeated until all water was consumed. The yield of ClO₂ was about 50% based on H₂¹⁸O. Incomplete hydrolysis of ClF₃ increased the ¹⁶O content by completing the hydrolysis on the glass walls of the vacuum line. We obtained samples of ClO₂ containing ca. 70–95% ¹⁸O.

AlCl₃ was prepared from the elements and used without further purification. Commercial BCl₃, HCl, NOCl, and Cl₂ (Merck) were purified by fractional condensation before use. Neon (99.999%, Linde) and argon (99.9999%, Messer-Griesheim) were used as matrix material without further purification.

Instrumentation. Details of the matrix-isolation apparatus are given elsewhere.³² The stopped flow apparatus for UV spectroscopic and kinetic investigations of ClClO₂ in the gas phase is described in greater detail in ref 33. This apparatus was coupled with a quartz glass cell

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Table I. Vibrational Frequencies (cm⁻¹)^a of Selected Isotopomers of Chloryl Chloride, ClClO₂, Isolated in a Neon Matrix, Relative Band Strength *I*,^b Gas Phase Band Positions (cm⁻¹), PR Separation (cm⁻¹), and Assignment

vibrational frequencies in a neon matrix								<i>I</i>	gas phase	$\Delta\nu$ (PR)	assignment
³⁵ Cl ³⁵ Cl- ¹⁶ O ₂	³⁷ Cl ³⁵ Cl- ¹⁶ O ₂	³⁵ Cl ³⁷ Cl- ¹⁶ O ₂	³⁷ Cl ³⁷ Cl- ¹⁶ O ₂	³⁵ Cl ³⁵ Cl- ¹⁸ O ₂	³⁷ Cl ³⁵ Cl- ¹⁸ O ₂	³⁵ Cl ³⁷ Cl- ¹⁸ O ₂	³⁷ Cl ³⁷ Cl- ¹⁸ O ₂				
2421.33	2421.33			2340.67	2340.67	2313.93	2313.93	0.3			2ν ₅ (a')
2242.57	2242.57	2222.80	2222.80	2160.20	2160.20	2139.40	2139.40	2.0	2246	12	ν ₁ + ν ₅ (a'')
2073.83	2073.83	2059.03	2059.03	1988.97	1988.97	1974.00	1974.00	1.8	2072		2ν ₁ (a')
1216.37	1216.37	1203.50	1203.50	1175.70	1175.70	1162.33	1162.33	100	1218.2	12.7	ν ₅ = ν _{as} (ClO ₂) (a'')
1044.73	1044.73	1037.23	1037.23	1004.03	1004.03	995.80	995.80	29			2ν ₂ (a')
									1041.5	15.5	
1041.20	1041.20	1033.80	1033.80	998.40	998.40	990.83	990.83	74			ν ₁ = ν ₅ (ClO ₂) (a')
522.50	522.50	518.50	518.50	502.37	502.37	498.10	498.10	9.4	522.7		ν ₂ = δ(ClO ₂) (a')
440.43	439.30	433.43	432.30	432.70	431.57	425.80	424.67	82	440.5	15.2	ν ₃ = δ(ClCl ₂ O ₂) (a')
271.37	267.17	271.37	267.17	265.93	261.77	265.93	261.77	7.0			ν ₄ = ν(Cl ₁₇ ClO ₂) (a')
251.40	250.17	250.63	249.40	241.4	240.2	240.6		0.34			ν ₆ = ρ(ClO ₂) (a'')

^a Accuracy: see text. ^b ClCl¹⁶O₂ isotopomers, see text; *I*(ν₅) = 100.

(optical path length 2.0 and 10.0 cm, respectively), equipped with quartz glass windows (Suprasil, Hellma).

Matrix infrared spectra were recorded with the FTIR spectrometer IFS 66 v (Bruker) operating in reflection mode between 4000 and 200 cm⁻¹ with an apodized resolution of 0.3 cm⁻¹. Gas-phase infrared spectra were obtained using the FTIR spectrometer MX-1 (Nicolet) operating between 4800 and 400 cm⁻¹ with a resolution of 2 cm⁻¹ using a 17-cm glass cell equipped with IR grade silicon windows (Wacker-Chemie).

Ultraviolet spectra were measured using a Diode-Array spectrometer system (Spectroscopy International) between 220 and 800 nm with a spectral resolution of 0.4–1 nm.

Photolysis experiments with matrix-isolated ClClO₂ were undertaken with a Hg medium-pressure lamp TQ 150 (Heraeus), a 1:1 quartz glass optic, and cut-off filters GG 395, GG 455, and GG 495 (Schott). For photolysis of Cl₂/ClO₂ mixtures, a 150-W tungsten halogen lamp combined with the above mentioned cut-off filters was used.

Isolation of ClClO₂ in Noble Gas Matrices. Prior to use, the stainless steel vacuum system of the matrix isolation apparatus was passivated with ClF₃. Mixtures of FClO₂/Ne (FClO₂/Ar) 1:500 were passed over AlCl₃ in a U-trap at 270 K, followed by quenching the reaction products in a matrix on a metal mirror at 5 K (11 K). Four experiments were undertaken with argon (0.5, 1.6 twice, and 1.8 mmol matrix with a deposition rate of 3 mmol h⁻¹) and one with neon (0.9 mmol matrix, ca. 5.5 mmol h⁻¹) to obtain spectra in the mid-IR region. One of the argon matrices (1.6 mmol) was also investigated for recording far-IR spectra.

In a second set of experiments a device as shown in Figure 1 was used instead of the U-trap. Two experiments were undertaken with argon (2.2 mmol matrix each, deposition rate 2 and 3 mmol h⁻¹, respectively); for another two experiments ¹⁸O-enriched FClO₂ was used (1.9 and 3.0 mmol Ar matrix, ca. 3 mmol h⁻¹). FClO₂/Ne (1.8 mmol) and ¹⁸O-enriched FClO₂/Ne (2.0 mmol) were deposited in two further experiments with a deposition rate of 5.5 mmol h⁻¹. The Ne matrices were used to record mid-IR, far-IR, and UV spectra.

Synthesis of ClClO₂ for Gas-Phase Studies. Passage of FClO₂ at low pressure (0.1–1 mbar) over AlCl₃ followed by collection of the products at 77 K in a U-trap for several minutes and rapid warming of the frozen products to room temperature allowed the detection of traces of ClClO₂ by its three strongest IR bands (see below). For this heterogeneous reaction the main products were ClO₂ and unreacted FClO₂.

Homogeneous reactions of FClO₂ with either BCl₃ or HCl in the gas phase were also attempted, and both reactions were found to be well suited for the synthesis of ClClO₂. Best results were obtained when a few millibar or less of these compounds in a 1:1 to 2:1 ratio were mixed in a reactor for a few seconds before the reaction products were passed through the absorption cell. As ClClO₂ has some stability at room temperature, spectroscopic and kinetic investigations may also be undertaken in a stopped-flow system or even in a static system.

Reaction of FClO₂ with ClNO gave very little ClClO₂; ClNO₂ was observed as the main product. Attempts to isolate pure ClClO₂ by fractional condensation failed. The reaction of FClO₂ with an excess of HCl at ~160 K yielded only HF, ClO₂, and Cl₂ as products, in accordance with ref 27.

Results and Discussion

IR Spectra of ClClO₂ Isolated in Noble Gas Matrices and Vibrational Assignment. Both IR and UV spectra showed bands due to ClO₂ and a novel chlorine oxide, which could be clearly identified as ClClO₂ by comparison with spectra of related molecules. No ClO₂ was detected in the spectra of noble gas/FClO₂ precursor mixtures. Only in the last experiment of the

Table II. Anharmonic Fundamental Frequencies (cm⁻¹) of Selected Chlorine Compounds

FCl ^{a,d}	ClCl ^{a,e}	assignment	
773.499	554.35	ν(XCl)	
FClO ^{b,f}	ClClO ^{b,g}	ClO ^{a,h}	assignment
1038.0	961.8	842.565	ν(ClO)
593.5	375.1		ν(XCl)
315.2	239.4		δ(XClO)
FClO ₂ ^{a,i}	ClClO ₂ ^c	ClO ₂ ^{a,j}	assignment
1105.8	1041.20	945.592	ν ₅ (ClO ₂)
546.5	522.50	447.68	ν(ClO ₂)
630.2	440.43		ν(FCl)/δ(ClCl ₂ O ₂) ^k
401.6	271.37		δ _s (FClO ₂)/ν(Cl ₁₇ ClO ₂) ^k
1271.4	1216.37	1110.105	ν _{as} (ClO ₂)
367.0	251.40		ρ(ClO ₂)

^a Gas phase values. ^b Argon matrix values. ^c Neon matrix values, this work. ^d Reference 34. ^e Reference 35. ^f Reference 36. ^g Reference 18. ^h Reference 37. ⁱ Reference 38. ^j Reference 39. ^k See text.

second run (FCl¹⁶O₂/Ne) were bands of FClO₂ observed. From integrated band intensities in the gas phase (see below), we estimated the ClClO₂/ClO₂ ratio to be always very close to 1:1, independent of the deposition assembly used. ClClO₂ was isolated in a neon matrix as well as in an argon matrix in order to distinguish between matrix and isotopic splittings in the IR spectrum. All six fundamental vibrations as well as some overtones and combination bands of 12 isotopomers were measured and are in agreement with the expected C_s symmetry of the ClClO₂ molecule

$$\Gamma_{\text{vib}} = 4a'(\text{IR, Ra p}) + 2a''(\text{IR, Ra dp})$$

Frequencies and relative intensities of selected isotopomers isolated in a neon matrix are listed in Table I; gas-phase data and assignments are included. Band positions of ¹⁶/¹⁸O mixed species and of ClClO₂ isolated in an argon matrix are available as supplementary material. The uncertainty in the band positions of matrix-isolated ClClO₂ is 0.03 cm⁻¹, except for 2ν₅ and ν₆ where the uncertainty is 0.05 cm⁻¹ (for ν₆ of the ¹⁸O-containing species it is 0.1 cm⁻¹) because of low intensity, while for gas-phase bands it is 0.5 cm⁻¹. The uncertainty for the relative band intensities is between 5% for strong bands and 10% for weaker ones; for ν₃ it is 15% because of the sloping base line, and for 2ν₅ and ν₆ it is 25% because of low intensity. Differences in the relative intensities between certain isotopomers are within the limits of uncertainty, except for ν₁ and 2ν₂ because of Fermi resonance (see below). Details of IR spectra in the region of the fundamentals of ClCl¹⁶O₂ are shown in Figure 2. The bands were assigned by comparing band positions observed for FCl,³⁴ Cl₂,³⁵ FClO,³⁶ ClClO,¹⁸ ClO,³⁷ FClO₂,³⁸ and ClO₂³⁹ (cf. Table II). Isotopic

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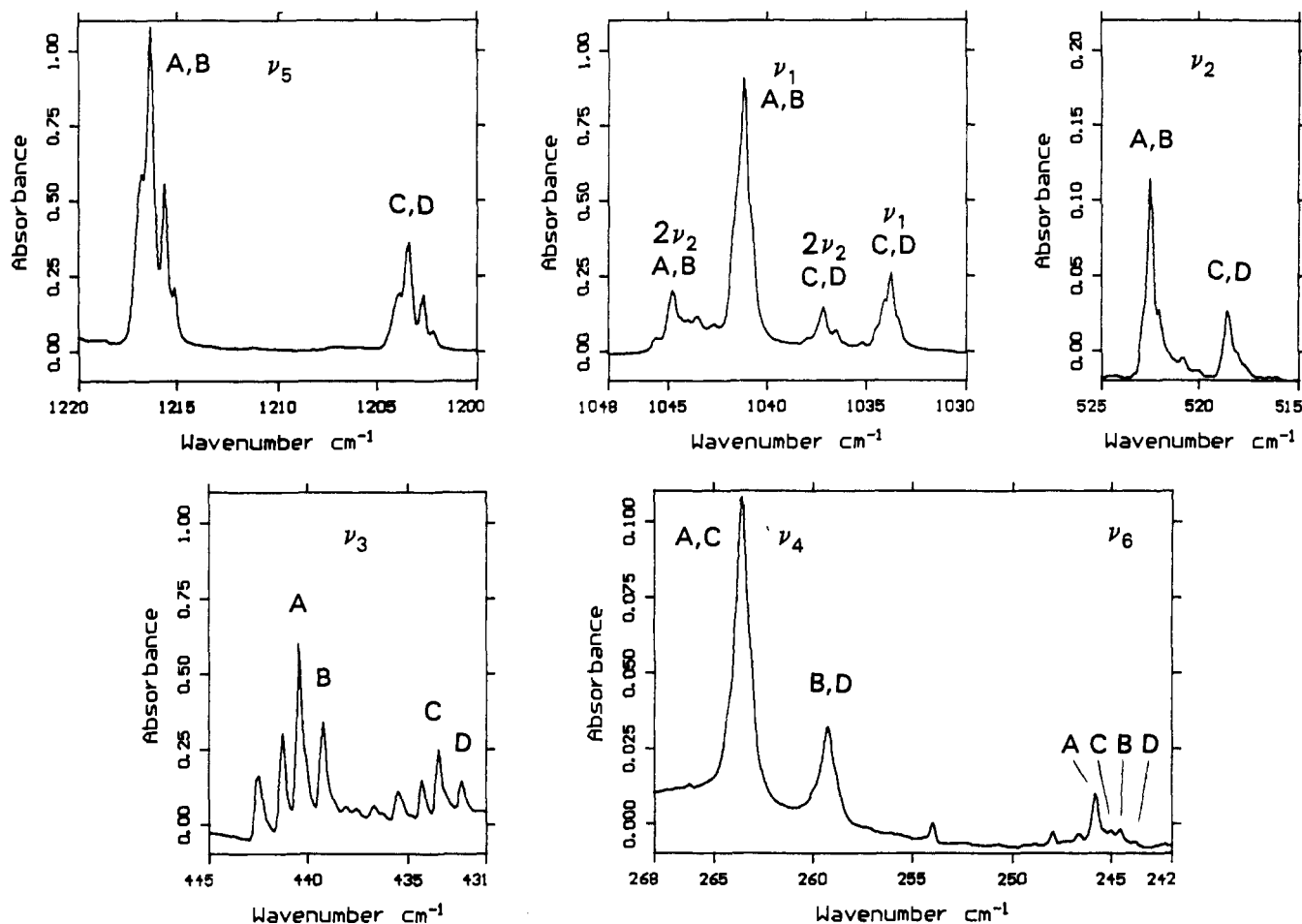


Figure 2. IR spectrum of $\text{ClCl}^{16}\text{O}_2$ isolated in a noble gas matrix in the regions of ν_5 , $2\nu_2/\nu_1$, ν_2 , ν_3 (neon matrix), and ν_4/ν_6 (argon matrix, double amount); ν_3 and ν_5 show matrix splittings. The four isotopomers $^{35}\text{Cl}^{35}\text{ClO}_2$ (A), $^{37}\text{Cl}^{35}\text{ClO}_2$ (B), $^{35}\text{Cl}^{37}\text{ClO}_2$ (C), and $^{37}\text{Cl}^{37}\text{ClO}_2$ (D) are indicated. Note the different absorbance scaling.

shifts, gas-phase band contours, and relative intensities, as well as force field and ab initio calculations^{7,11-14} support this assignment.

Modes ν_1 , ν_2 , and ν_5 , Involving Mainly the ClO_2 Group. In FCIO_2 the fluorine atom decreases the electron density at the chlorine atom mainly in the antibonding orbitals. This strengthens the ClO bonds and causes a blue shift of the ClO_2 modes of FCIO_2 compared to those of ClO_2 . Because chlorine is less electronegative than fluorine, the ClO_2 modes of ClClO_2 should be positioned between those of FCIO_2 and ClO_2 , just as the ClO stretching vibration of ClClO is situated between that of FCIO and ClO . Hence bands near 1040, 520, and 1210 cm^{-1} (cf. Figure 2) are assigned to $\nu_1 = \nu_s(\text{ClO}_2)(a')$, $\nu_2 = \delta(\text{ClO}_2)(a')$, and $\nu_5 = \nu_{as}(\text{ClO}_2)(a'')$, respectively. For ν_1 , ν_2 , and ν_5 the isotopic shifts due to the terminal Cl atom are expected to be very small, and these isotopic splittings were not resolved in neon matrix spectra (cf. force field section).

Modes ν_3 , ν_4 , and ν_6 , Involving Mainly the Terminal Chlorine Atom. A group of bands near 245 cm^{-1} (cf. Figure 2) shows an intensity pattern of nearly 9:3:3:1 as expected for a molecule with two inequivalent chlorine atoms. By comparison with the band positions of ν_6 of FCIO_2 and the deformation modes of ClClO and FCIO (see Table II), these bands are obviously assigned to $\nu_6 = \rho(\text{ClO}_2)(a'')$.

The remaining modes ν_3 and ν_4 are observed near 440 and 260 cm^{-1} , respectively. The former group of bands also shows the

intensity pattern of about 9:3:3:1, indicating two inequivalent chlorine atoms (although matrix splitting causes a superposition of the bands, the intensity pattern could be identified), whereas in the latter group of bands only the isotopic splittings of the terminal chlorine atom were resolved; these bands are quite broad (half width ca. 0.7 cm^{-1}) due to overlapping of the $\text{Cl}^{35}\text{ClO}_2$ and $\text{Cl}^{37}\text{ClO}_2$ bands (see Table VII).

Comparing $^{35}\text{Cl}^{35}\text{ClO}_2$ (A) with the two species containing one ^{37}Cl atom (B, C), the greater chlorine isotopic shift of ν_3 and ν_4 is due to $^{35}\text{Cl}^{37}\text{ClO}_2$ (C) and $^{37}\text{Cl}^{35}\text{ClO}_2$ (B), respectively, as shown by ab initio^{7,8,11} and force field calculations. (Unlabeled atoms always indicate both isotopes, $^{16}/^{18}\text{O}$ or $^{35}/^{37}\text{Cl}$.) Comparison with similar modes in XXY and XXY_2 molecules support these assignments. In a bent XXY or pyramidal XXY_2 molecule with $\angle(\text{XXY}) \approx 100^\circ$ usually the central X atom shows a greater isotopic shift of the XX stretching vibration than the terminal X atom, while it is opposite for the symmetrical deformation mode. This was measured or derived from experimental force fields for HO_2 ,⁴⁰ O_2F ,⁴¹ ClClO ,¹⁸ SSF_2 ,⁴² and SeSeF_2 ,⁴³ (Note that the magnitudes of the X isotopic shifts for $\nu(\text{XX})$ and $\delta(\text{XXY})$ are opposite for linear molecules like N_2O ⁴⁴ and C_2O .⁴⁵) Correspondingly and in comparison to the assignments given in Table II, ν_3 and ν_4 of ClClO_2 might be described as $\nu(\text{ClCl})$ and δ -

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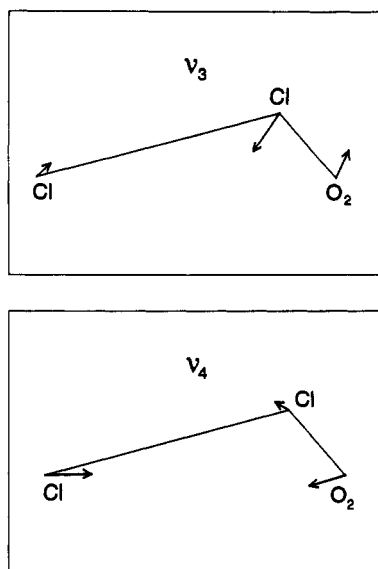


Figure 3. Cartesian displacement of the normal coordinates of ν_3 and ν_4 of ClClO_2 (projection into the C_s plane; the vectors are lengthened for clearness).

(Cl–ClO₂), respectively. But force field calculations (see below) indicate the description of ν_3 and ν_4 in terms of internal coordinates to be more complex. These vibrations are mixed, and according to the Cartesian displacement of the eigenvectors, ν_3 and ν_4 are best described as vibrations of the central (C), and terminal (T), chlorine atoms with respect to the rest of the molecule (cf. Figure 3). This can be symbolized as $\nu_3 = \delta(\text{Cl}–\text{Cl}_C–\text{O}_2)$ and $\nu_4 = \nu(\text{Cl}_T–\text{ClO}_2)$.

Overtone and Combination Bands. The overtones $2\nu_2$ and $2\nu_4$ were observed as relatively intense bands because of their enhancement by Fermi resonance with ν_1 and ν_2 , respectively. Figure 2 clearly shows that the features to the higher frequency side of the ν_1 bands cannot be due to matrix splittings because of their different band shapes and relative intensities. While $2\nu_2$ is strong both in neon and argon matrices, the intensity of $2\nu_4$ and its perturbation of ν_2 is significant only in an argon matrix. The ¹⁶O species exhibit a stronger perturbation of both overtones than the ¹⁸O species (cf. Table I; $I(\nu_1) = 91$ and $I(2\nu_2) = 3.5$ for $\text{ClCl}^{18}\text{O}_2$). The corrections of ν_1 because of Fermi resonance are estimated to be 0.8, 1.03, 0.20, and 0.17 cm^{-1} for $\text{Cl}^{35}\text{Cl}^{16}\text{O}_2$, $\text{Cl}^{37}\text{Cl}^{16}\text{O}_2$, $\text{Cl}^{35}\text{Cl}^{18}\text{O}_2$, and $\text{Cl}^{37}\text{Cl}^{18}\text{O}_2$, respectively, by comparing relative intensities of ν_1 and $2\nu_2$.⁴⁶

Although $2\nu_4$ could not be detected for the ¹⁸O-containing species isolated in an Ar matrix, its presence caused appearance of separate bands for ³⁵ClClO₂ and ³⁷ClClO₂ in ν_2 .

$2\nu_5$, $\nu_1 + \nu_5$, and $2\nu_1$ were observed in the expected regions with relative intensities (cf. Table I) similar to those of the corresponding vibrations of FClO₂ and ClO₂.

IR Spectrum of ClClO₂ in the Gas Phase. ClClO₂ is an asymmetrical rotator ($\kappa \approx -0.76$) of the prolate type as can be concluded from the derived geometric parameters (see below). According to ref 47, band contours and PR separation can be calculated. Type A bands should show PQR structure with $\Delta\nu(\text{PR}) \approx 16.2$. With $\rho \approx 2.0$ type B bands ($\Delta\nu(\text{PR}) \approx 13.0 \text{ cm}^{-1}$) should resemble PR more than PQQR contours, and type C bands (24.2 cm^{-1}) Gaussian more than PQR contours. a' bands of ClClO₂ are hybrid bands of AC type while a'' bands are of B type. The uncertainty in rotational constants, overlap of several ^{35/37}Cl isotopomers, and the presence of hot bands may account for deviations between measured and calculated PR separations.

The three strongest bands $\nu_1/2\nu_2$, ν_3 , and ν_5 were observed in the gas-phase IR spectra of ClClO₂ with positions and relative intensities close to those observed in a neon matrix. ν_5 (1218.2

Table III. Comparison between Measured^a and Calculated^b Vibrational Frequencies (cm^{-1}) and Relative Intensities^c of ³⁵Cl³⁵Cl¹⁶O₂

	expt ^a	HF 3-21G* ^d	MP 2 6-31G**	CISD 6-31G* ^a	CCSD DZP ^f
ν_1	1041 (103 ^g)	1012 (174)	1190 (16.6)	1124 (108)	978 (94)
ν_2	523 (9.4)	557. (28)	490 (24.3)	535 (15.9)	482 (14.7)
ν_3	440 (82)	468 (120)	359 (46.5)	453 (63)	436 (61)
ν_4	271 (7.0)	259 (47)	197 (9.6)	268 (18.9)	266 (6.7)
ν_5	1216 (100)	1262 (100)	1350 (100)	1311 (100)	1136 (100)
ν_6	251 (0.34)	273 (5.4)	185 (2.8)	263 (2.5)	236 (2.6)

^aAnharmonic frequencies, neon matrix values, this work, cf. Table I. ^bHarmonic frequencies. ^c $I(\nu_3) = 100$. ^dReference 13. ^eReference 7. ^fReference 11. ^g $I(\nu_1) + I(2\nu_2)$, see Table I and text.

cm^{-1} , $\Delta\nu(\text{PR}) = 12.7 \text{ cm}^{-1}$) shows PR contours, while $\nu_1/2\nu_2$ (1041.5 cm^{-1} , $\Delta\nu(\text{PR}) = 15.5 \text{ cm}^{-1}$) and ν_3 (440.5 cm^{-1} , $\Delta\nu(\text{PR}) = 14.7 \text{ cm}^{-1}$) all clearly show the expected PQR structure (a survey spectrum is presented in ref 48).

In the reaction products obtained from FClO₂/BCl₃ and FClO₂/HCl mixtures, two weak bands were observed at 522.7 and 518.5 cm^{-1} . They are most likely assigned to the Q-branches of ν_2 of $\text{Cl}^{35}\text{ClO}_2$ and $\text{Cl}^{37}\text{ClO}_2$, respectively.

The combination band $\nu_1 + \nu_5$ (2246 cm^{-1} , $\Delta\nu(\text{PR}) \approx 12 \text{ cm}^{-1}$) was observed with a band contour similar to that of ν_5 , as expected.

The overtone $2\nu_1$ is situated near 2072 cm^{-1} . There is some uncertainty in the exact position of this band because it is partially overlapped by the strong $\nu_1 + \nu_3$ band of ClO₂.

In order to allow estimation of the integral band intensities of ClClO₂, kinetic experiments (stopped flow) have also been undertaken. Assuming ClO₂ and Cl₂ to be the only decomposition products of ClClO₂ and the formation of ClO₂ to be due only to decomposition of ClClO₂, we determined the intensity ratio of $\nu_{\text{as}}(\text{ClO}_2)$ of ClClO₂ and ClO₂ to be about 2.1:1.

Vibrational frequencies and intensities were calculated with ab initio methods. At the HF/3-21G* level¹³ experimental and calculated frequencies agree well (average deviation 5.5%), while some deviations are observed in the relative intensities (cf. Table III). With MP2 calculations, poorer agreement is obtained; the average deviation is 17.3, 17.2, and 15.9% for the 6-31G*,^{7,12,13} 6-311G*,¹³ and D95*¹³ basis sets, respectively. At the CCSD/DZP¹¹ and the CISD/6-31G* level¹³ calculated frequencies (average deviation 4.9 and 4.4%, respectively) as well as relative intensities correspond well to the experimental ones.

The UV spectrum of ClClO₂ isolated in a neon matrix shows two unstructured bands with maxima at 236 and 296 nm with equal intensity and half-widths of ~ 40 and ~ 45 nm, respectively.²⁹

Kinetic investigations of the FClO₂/BCl₃ reaction in the gas phase have been undertaken to investigate the decomposition and the UV-vis spectrum of ClClO₂. The UV spectrum of ClClO₂ in the gas phase is very similar to that in a neon matrix: Two maxima are observed at 231 and 296 nm with $\sigma = 1.3$ and $1.5 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, respectively ($\epsilon_0 = 3.4$ and $3.9 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). The minimum is at 261 nm with $\sigma = 5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ($\epsilon_0 = 1.4 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). The blue shift of the first maximum is due to interaction between ClClO₂ and the matrix material.

No maximum was observed above 300 nm. We estimate the absorption cross section between 500 and 800 nm to be below $10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$. Nevertheless, photolysis experiments of matrix-isolated ClClO₂ suggest it absorbs in the visible region (see below).

The uncertainty of the absorption cross section in the region of ~ 230 to ~ 330 nm is less than $\pm 20\%$. At higher wavelengths it is larger because of the weak absorption of ClClO₂, while at lower wavelengths our results (also the exact position of the first

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Table IV. Diagonal Force Constants^a (10² N m⁻¹) and Equilibrium Structural Parameters (pm, deg) of Selected Chlorine Compounds

	FCl ^b	ClCl ^c	
f_R/R	4.452/162.83	3.225/198.8	
	FClO ^d	ClClO ^e	ClO ^f
f_R/R	2.59/...	1.37/...	
f_i/r	6.85/...	5.94/...	4.713/156.96
f_α/α	0.92/...	0.78/...	
	FClO ₂ ^g	ClClO ₂ ^h	ClO ₂ ⁱ
f_R/R	2.574/169.4	1.245/222	
f_i/r	8.899/142.0	8.173/144	7.055/146.98
f_α/α	1.406/101.8	1.175/103.5	
f_β/β	2.025/115.3	1.702/116	1.382/117.40

^a $R = r(\text{ClCl})$ or $r(\text{FCl})$, $r = r(\text{ClO})$, $\alpha = \angle(\text{ClClO})$ or $\angle(\text{FClO})$, $\beta = \angle(\text{OCIO})$; deformation force constants normalized to 100 pm bond length. ^b Reference 50, f_{iR} derived from ref 34. ^c Reference 35. ^d Reference 36. ^e Reference 18. ^f Reference 51, f_i derived from ref 37. ^g Reference 52. ^h This work, structural parameters derived from vibrational frequencies, see text. ⁱ Reference 39.

band) might be affected by the decreasing energy of our UV spectrometer system.

Two very strong bands were predicted by ab initio methods at 243 and 358 nm, a weaker one at 224 nm and much weaker ones at 295, 473, and 481 nm.⁹ The two strongest bands might correspond to our measured ones. In ref 10 the corresponding positions were determined (without intensities) at 276, 358, 258, 332, 554, and 571 nm, mostly something red shifted compared to the calculations of ref 9.

Evaluation of Geometric Parameters. The use of the product rule in the symmetry class a''

$$\nu_5^2 \nu_6^2 / \nu_5'^2 \nu_6'^2 = \det(G) / \det(G')$$

(where prime denotes an isotopomer different from ³⁵Cl³⁵Cl¹⁶O₂; and G matrix elements are taken from ref 49), together with the vibrational frequencies of three independent pairs of isotopic molecules as input data (cf. Table I) allows the geometric parameters R/r , α , and β (see Table IV) to be estimated. Because the product rule is valid for harmonic frequencies, we used an anharmonic correction of 1.5% for the isotopic frequency shifts.⁵³ According to refs 35 and 54 $r(\text{ClO})$ could be estimated to be 144.0 ± 0.5 pm by comparing the arithmetical average of $\nu_6(\text{ClO}_2)$ and $\nu_{6s}(\text{ClO}_2)$ of ClClO₂, FClO₂, and ClO₂ with $r(\text{ClO})$ of FClO₂ and ClO₂. Roughly estimated values for R , α , and β of ClClO₂ were derived from Table IV and were refined in steps of 0.5 pm and 0.25° by trial and error, using the product rule. The following values were obtained: $R = 220$ pm, $\alpha = 101.5^\circ$, and $\beta = 116.0^\circ$. An OCIO bond angle of 116.0° is also suggested by comparison with the corresponding bond angles of FClO₂ and ClO₂. Ab initio calculations at the MP2/6-31G* level predict $\angle(\text{XClO})$ in ClClO₂ (104.2°) to be greater than in FClO₂ (102.0°). Taking the experimental value of 101.8° of FClO₂ (cf. Table IV), we would prefer $\angle(\text{ClClO})$ in ClClO₂ to be about 103.5°. This value affords $R = 222$ pm to give the best agreement with the experimental data. The uncertainties of the measured frequencies and the estimated anharmonicity correspond to an uncertainty of ±6 pm for R , while those of α and β are suggested to be 1° and 0.5°, respectively.

Precise geometric parameters can be deduced from microwave spectra which are presently being investigated.

Our estimated geometric parameters are supported by ab initio calculations: Good agreement is observed with values obtained at the HF/3-21G*,¹³ CISD/6-31G*,¹³ and CCSD/TZ2P¹¹ levels

Table V. Experimental and ab Initio Geometric Parameters (pm, deg) and Dipole Moment μ (D) of ClClO₂

	HF			CCSD		
	expt ^a	3-21 G* ^b	6-31 G* ^c	6-31 G* ^b	DZP ^d	TZ2P ^d
$r(\text{ClCl})$	222	218.5	245.9	221.6	224.0	222.1
$r(\text{ClO})$	144	144.1	146.9	144.7	148.8	145.1
$\angle(\text{ClClO})$	103.5	104.1	104.2	103.8	104.4	103.9
$\angle(\text{OCIO})$	116	114.8	116.7	114.8	114.2	114.4
μ		2.47	3.38	2.32	2.02	1.79

^a This work, from vibrational data, see text. ^b Reference 13. ^c Reference 7. ^d Reference 11.

(cf. Table V). Greater deviations are obtained when HF and MP2 calculations with 6-31G*, 6-311G*, and D95* basis sets are used;¹³ especially $r(\text{ClCl})$, obtained from HF calculations, is shorter (~212.5 pm), but when obtained from MP2 calculations, it is significantly longer (>241 pm) than our value of 222 pm. Except for $\angle(\text{OCIO})$, results at the CCSD level¹¹ agree better with our findings than those at the CCSD(T) level,¹⁴ and those with the larger TZ2P basis set agree better than those with the DZP basis set.^{11,14} Generally, calculated geometrical parameters and vibrational frequencies show similar deviations from our experimental values. It should be pointed out that the longer ClO bond lengths obtained from MP2 calculations^{7,12,13} are incompatible with their higher ClO stretching frequencies (cf. refs 35 and 54), while the ClO bond lengths obtained at the HF/3-21G*, CISD/6-31G*, and the CCSD/DZP level are compatible with their ClO stretching frequencies.

A normal coordinate analysis was undertaken to confirm the assignments and to obtain a better description of the bonding in ClClO₂. For the computation of the general valence force field the program NORCOR⁵⁵ was used with the structural parameters (see above), vibrational frequencies (cf. Table I), and an initial force field derived from related compounds (cf. Tables IV and VI) or from ab initio calculations (cf. Table VI) as input data. Instead of the measured frequencies of ν_1 the corrected ones were used because of Fermi resonance (see matrix IR spectrum section). For all isotopic shifts an anharmonic correction of 1.5% was applied.⁵³ Because of the uncertainties in ν_1 and ν_6 these frequencies were given a weighting of one-half in the force field calculation. Frequencies of ³⁷Cl isotopomers, for which we have not measured an isotopic shift, were given a weighting according to their shift expected from ab initio calculations.¹²⁻¹⁴ The best result together with the potential energy distribution is given in Table VI. Values of ClClO₂ from ab initio calculations,^{13,14} as well as experimental ones of FClO₂,⁵² are included.

Several calculations showed most of the force constants to be well determined from our input data, independent of the initial force constants; the deviation is less than ±3 in the last digit, whereas the uncertainty for $f_{r\alpha} + f_{r\alpha'}$ and for $f_{r\beta}$ is nearly ±10 in the last digits. The force field might be improved if the exact geometric parameters of ClClO₂, a better correction for Fermi resonances, the harmonic frequencies, and centrifugal distortion constants were used in the calculation.

Most of the vibrational frequencies were reproduced within or near the experimental error. The input isotopic shifts and those from the force field calculation are listed in Table VII. In the case of deviations greater than 0.1 cm⁻¹, the band positions were reproduced better than the isotopic shifts.

The potential energy distribution for the different isotopomers are very similar, differences for the main contributions are mostly below 0.03. Some contributions for ³⁷Cl³⁷Cl¹⁶O₂/³⁵Cl³⁵Cl¹⁸O₂ show greater deviations: ν_2 , 0.80 $f_\beta/0.71f_\beta$; ν_3 , 0.38 $f_\alpha/0.32f_\alpha$, and 0.18 $f_\beta/0.26f_\beta$.

Whereas ν_1 , ν_5 , ν_6 , and even ν_2 of ClClO₂ can be considered to be characteristic vibrations, ν_3 and ν_4 are mixed (see above). The potential energy distribution (PED) of ν_3 can be rationalized

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Table VI. Force Constants^a (10² N m⁻¹) of ClClO₂ and FClO₂, and Potential Energy Distribution (PED)^b of ClClO₂

	ClClO ₂				FClO ₂ expt ^f	PED ^c					
	expt ^c	HF/3-21G ^{*d}	CISD/6-31G ^{*d}	CCSD/DZP ^e		ν ₁	ν ₂	ν ₃	ν ₄	ν ₅	ν ₆
f _R	1.246	1.051	1.110	1.242	2.574			0.23	0.69		
f _r	8.167	8.339	9.559	7.181	8.899	1.00				0.97	
f _α	1.175	1.456	1.298	1.146	1.406		0.14	0.37	0.24		1.54
f _β	1.702	2.173	1.957	1.730	2.025		0.78	0.20			
f _{Rr}	-0.135	0.455	0.237	0.104	-0.192						
f _{Rα}	-0.011	0.001	0.052	-0.018	0.052						
f _{Rβ}	-0.042	-0.071	-0.333	-0.090	0.153						
f _{rr}	-0.263	-0.813	-0.255	-0.204	-0.064						
f _{ra}	0.034	0.032	0.003	-0.006	0.080						
f _{ra}	-0.101	-0.201	-0.109	-0.080	0.299						
f _{rβ}	0.057	0.096	0.045	0.064	0.157						
f _{αα}	0.412	0.565	0.457	0.441	0.270			0.13			
f _{αβ}	0.102	0.490	0.126	0.391	0.195						-0.54

^a Deformation force constants normalized to 100 pm bond length. ^b ³⁵Cl³⁵Cl¹⁶O₂ isotopomer, see text; only contributions of ≥0.1 are presented. ^c This work. ^d Reference 13. ^e Reference 14. ^f Reference 52.

Table VII. Comparison of Measured^a Isotopic Shifts Δν^b (cm⁻¹) with Those from Experimental Force Field Calculation

	Δν(Cl _T)		Δν(Cl _C)		Δν(O)	
	obsd	calcd	obsd	calcd	obsd	calcd
ν ₁	0	0.02	7.28	7.10	44.05	44.11
ν ₂	0	0.24	4.06	4.09	20.43	20.48
ν ₃	1.15	1.19	7.10	7.16	7.85	7.97
ν ₄	4.26	4.34	0	0.48	5.52	5.63
ν ₅	0	~10 ⁻⁴	13.06	13.18	41.28	41.40
ν ₆	1.25	1.23	0.78	0.83	10.15	10.08

^a Including harmonic correction, see force field section. ^b Δν(Cl_T) = ν(³⁵Cl³⁵Cl¹⁶O₂) - ν(³⁷Cl³⁵Cl¹⁶O₂), Δν(Cl_C) = ν(³⁵Cl³⁵Cl¹⁶O₂) - ν(³⁵Cl³⁷Cl¹⁶O₂), Δν(O) = ν(³⁵Cl³⁵Cl¹⁶O₂) - ν(³⁵Cl³⁵Cl¹⁸O₂).

by the contribution of f_{XCl} to the PED of the following molecules: FClO (0.95), ClClO (0.83), and FClO₂ (0.67). The contribution of the ClCl stretching to ν₃ of ClClO₂ is 0.23 and fits well within this series. The contributions of f_{XClO} to δ_s(XClO) of FClO (0.96), ClClO (0.84), and FClO₂ (0.60) and to ν₄ of ClClO₂ (0.24) form a similar trend.

In Table IV the diagonal force constants are compared with those of related compounds. The ClCl stretching force constant of ClClO₂ is slightly smaller than in ClClO, very similar to the situation of FClO₂ and FClO. The other diagonal force constants are very close to values one would expect from the comparison mentioned above.

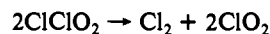
Considering the different bonding, the interaction force constants of ClClO₂ and FClO₂ agree quite well. Greater deviations may be due to the poorer reproduction of the measured frequencies of FClO₂ and the large uncertainties in the force constants (cf. ref 52). The ab initio force constants of ClClO₂ (cf. Table VI) and the experimental ones agree reasonably well in the HF/3-21G^{*}, better in the CISD/6-31G^{*}, and very well in the CCSD/DZP case. The sign of f_{Rr} should be negative, because increase of electron density at the central Cl atom due to ClCl bond lengthening weakens the ClO bond.

Calculated isotopic shifts, scaled by ν_{measd}/ν_{calcd}, correspond well to the measured isotopic shifts of ν₁, ν₂, ν₃, and ν₆. Some deviations are observed for Δν(Cl_T), Δν(Cl_C), and Δν(O) of ν₃ and ν₄, respectively, e.g. at the CCSD/DZP level,¹⁴ 1.60, 7.24, 7.11 cm⁻¹ and 4.16, 0.31, 6.38 cm⁻¹, while the agreement is better at the MP2/6-31G^{*} level,¹² 1.0, 7.2, 7.9 cm⁻¹ and 4.5, 0.5, 5.1 cm⁻¹ (see also Table VII). The isotopic shifts are strongly correlated with the potential energy distribution and with the description of the normal modes. Correspondingly at the CCSD/DZP level ν₃ and ν₄ show higher stretching and bending contributions, respectively, compared to our force field calculations, while it is opposite for the MP2/6-31G^{*} level.

Chemical Behavior. Stopped flow experiments of the reaction between BCl₃ and FClO₂ (mostly 1:1, 0.5–12 mbar each) were examined at room temperature. The reaction of FClO₂ with excess of BCl₃ was also studied; in this case FClO₂ was diluted with N₂ to adjust the pressure in the storage flask. Formation of ClClO₂

seems to follow first order in FClO₂ as well as in BCl₃ and is quite slow: Starting with ~1.0 mbar each, a maximum partial pressure of ClClO₂ (~0.6 mbar) is observed after 15 s.

Only ClO₂ could be detected as decomposition product of ClClO₂ by IR and UV spectroscopy (the absorption of Cl₂ around 330 nm is too weak to be detected). Decomposition of ClClO₂ follows approximately second order with a half-life of 60 s at ~1.0 mbar ClClO₂ and 4 mbar total pressure, suggesting to proceed via

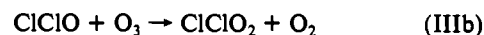


Another formation path of ClClO₂ was found by the reaction of photolytically generated chlorine atoms with ClO₂. When mixtures of Cl₂ and ClO₂ were irradiated at room temperature with a tungsten halogen lamp (λ ≥ 495 nm), simultaneous measurements show the only product besides ClO₂ which could be observed IR spectroscopically to be ClClO₂. Investigations of ClClO₂ in the gas phase will be discussed in greater detail in ref 48.

Irradiation of matrix-isolated ClClO₂ with visible light (λ ≥ 495 nm) for 10 min caused the concentration of ClClO₂ to decrease by 25%, while ClO₂ was nearly unaffected. Weak new IR bands were observed around 990 cm⁻¹, due to ClOClO,¹⁸ and weaker ones near 645 and 750 cm⁻¹, due to ClOOCl.^{22,23} After irradiation for another 10 min with λ ≥ 395 nm, half of the ClClO₂ and nearly all of the ClO₂ were decomposed. The above mentioned bands of ClOClO and ClOOCl increased and additional very strong bands of ClOO⁵⁶ were detected at 1442.6 and 1416.5 cm⁻¹, as well as a weak band at 542.8 cm⁻¹.

These results suggest that some of the matrix-isolated ClClO₂ is photolytically rearranged to ClOClO and ClOOCl, while ClO₂ is isomerized to ClOO. A more extended analysis of these photolysis experiments will be presented elsewhere.⁵⁷

Significance of ClClO₂ in the Stratosphere. The following reactions may lead to ClClO₂ in the atmosphere:



According to our results, ClClO₂ is expected to be stable under stratospheric conditions but will be readily photolyzed after sunrise. Therefore, ClClO₂ could be a source of stratospheric ClO₂, if schemes III are of importance. Although theoretical calculations on the ClO dimerization,^{10,15} especially when performed on a higher level, showed that ClClO₂ could be of importance in the ClO cycle, only spectroscopic investigations can evaluate the importance of ClClO₂ in the ClO dimerization process. Referring

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to eq IIIa, there is nothing known about ClClO in the gas phase yet.

Reaction II should be taken into consideration as a source of stratospheric ClClO₂ if this reaction is very fast; but it is more likely that Cl atoms will be consumed in the reaction with the much more abundant O₃, CH₄, etc. Nevertheless, this reaction should be considered in kinetic and spectroscopic investigations involving ClO₂ and Cl atoms.

If the photolytic decomposition of ClClO₂ to a Cl atom and ClO₂ in the electronic ground state were the most important reaction of this species under stratospheric conditions, its influence on ozone depletion would be small, although ClClO₂ might have a significant concentration in the stratosphere. Photolytic decomposition of ClO₂ into ClO + O would neutralize the Cl atom generated before. If on the other hand photolysis of ClClO₂ proceeded via electronic excited ClO₂ and a Cl atom, isomerization of ClO₂ to ClOO with subsequent decomposition into Cl + O₂ could contribute to ozone destruction.⁵⁸

Conclusion

We have synthesized chloryl chloride for the first time according to four different routes. This novel chlorine oxide is of sufficient

stability at room temperature and low pressure to allow its characterization by IR and UV spectroscopy not only in cryogenic matrices but also in the gas phase.

Comparison of its IR spectrum with those of related compounds showed this spectrum to fit a general trend and allowed us to estimate geometric parameters for ClClO₂. Our spectroscopic findings allow the identification of ClClO₂ in mixtures of chlorine oxides. Results of ab initio calculations were useful for analyzing and interpreting our experimental results, although significant deviations were observed even for higher level calculations.

ClClO₂ is thermally quite stable but is easily decomposed by irradiation with visible light. These properties are necessary conditions that ClClO₂ might play a role in the chemistry of the polar stratosphere. Nevertheless, further investigations are necessary to evaluate its importance there.

Acknowledgment. We thank T. J. Lee, H. G. Mack, and J. Oddershede for providing us their ab initio calculations, which are unpublished yet. Support by the Bundesminister für Forschung und Technologie (BMFT, Project No. VOZ08), the Deutsche Forschungsgemeinschaft (DFG), and Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: Tables of vibrational frequencies for ClCl¹⁶O₂ and ClCl¹⁸O₂ isolated in an Ar matrix and of ClCl¹⁶O¹⁸O and IR spectra of ClClO₂ in the regions of $\nu_1/2\nu_2$ and $\nu_2/2\nu_4$ (4 pages). Ordering information is given on any current masthead page.

- (58) (a) Vaida, V.; Solomon, S.; Richard, E. C.; Rühl, E.; Jefferson, A. *Nature* 1989, 342, 405. (b) Bishenden, E.; Haddock, J.; Donaldson, D. *J. J. Phys. Chem.* 1991, 95, 2113.

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Synthesis of ω -(Aminoalkyl)-1,2-closo-dicarbododecaboranes(12)

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Received December 2, 1991

Hydrogen chlorides of four 1,2-dicarba-closo-dodecaborane(12) derivatives containing ω -(aminoalkyl) substituents, namely 1-(aminomethyl)-, 1-(3-aminopropyl)-, 1-(3-aminopropyl)-2-methyl-, and 1,2-bis(3-aminopropyl)-1,2-dicarba-closo-dodecaborane(12) (1-4, respectively), were synthesized via deprotection of the corresponding *N,N*-di-*tert*-butyloxycarbonyl derivatives (8, 9, 16, and 19, respectively) using hydrogen chloride in anhydrous ether. The salt 1 was also obtained from its mono *N-tert*-butyloxycarbonyl derivative 7. The diprotected compounds 9, 16, and 19 were synthesized from the corresponding bromides by ion-pair alkylation of the Gabriel reagent di-*tert*-butyl iminodicarboxylate (6) using a stoichiometric amount of tetrabutylammonium hydroxide in the two-phase system water/methylene chloride. No degradation of the carborane cage to the nido compounds was observed. Alkylation of 6 with propargyl bromide gave *N,N*-di-*tert*-butyloxycarbonylpropargylamine (5), which upon reaction with the bisacetonitrile complex of decaborane gave a mixture of 7 and 8.

Introduction

It has recently been shown¹ by members of our research group that epidermal growth factor (EGF) when conjugated to dextran binds to cultured human malignant glioma, U343MGaC12:6, cells. The binding is receptor specific, most of the conjugate is located intracellularly, and the conjugate remains cell-associated for more than 24 h. Thus, it seems promising to use dextran, conjugated with EGF, as a carrier for toxic agents. We are presently examining the possibility of combining EGF-dextran targeting with boron neutron capture therapy (BNCT),² and for that purpose we are preparing boron cluster compounds, amino acids, and amines, for coupling to the dextran in the EGF-dextran conjugates.

Here we report the synthesis of the hydrogen chlorides of four ω -(aminoalkyl)-substituted 1,2-dicarba-closo-dodecaboranes(12) (*o*-carboranes): 1-(aminomethyl)-, 1-(3-aminopropyl)-, 2-(3-

aminopropyl)-1-methyl-, and 1,2-bis-(3-aminopropyl)-*o*-carborane (1-4, respectively).

Experimental Section

General Details. The ¹H, ¹³C, and ¹¹B NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 96.2 MHz, respectively. Boron fluoride etherate was used as external standard for the boron spectra. The IR spectra were obtained with a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra were recorded on a Finnigan Mat INCOS 50 instrument in the electron-impact mode or on a Jeol DX-303 instrument connected to a Jeol DA-5000 computer system for FAB spectrum. The fast atom bombardment spectra were recorded at a resolution set to 3000. The samples were prepared of a methanol solution of the compound with PEG 400 on the stainless steel target. The fast atom bombardment gun was operated at 6 kV producing a beam of xenon neutrals. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, FRG, and Mikrokemi AB, Uppsala, Sweden.

Merck Silica Gel 60 (230-400 mesh) and Merck Silica Gel 60 F₂₅₄ were used for flash chromatography and TLC, respectively. Melting points are uncorrected and were obtained using a Buchi capillary melting point apparatus or a Leitz hot-stage microscope. "Q*" is used for the tetrabutylammonium ion.

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(2) For a recent review of BNCT, see: Barth, R. F.; Soloway, A. H.; Fairchild, R. G. *Cancer Res.* 1990, 50, 1061.